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(54) PRODUCTION OF CARBON NANOTUBE

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain carbon nanotube excellent in directionality on a base substance selected from a wide range of materials at a relatively low temperature by previously forming the carbon nanotube-growing areas on the surface of the base substance, arranging the areas in the reaction vessel, introducing the starting gas and generating plasma by direct current glow discharging.
SOLUTION: On the surface of a base substance 43 (for example, Pd base plate) which is also used as a cathode for direct current glow discharge, are previously formed the carbon nanotube-growing areas that is formed preferably by changing physically the shapes or chemically the composition of the areas, more preferably by forming metallic ultrafine particles containing any of Fe, Co or Ni. Then, the base substance is arranged on the base holder equipped with a heater 44 in the reactor vessel 41 and the starting gas for introduction of carbon (for example, ethylene, He and H2) is introduced and plasma is generated by the direct current glow discharge in the reactor vessel.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the carbon nanotube characterized by to form a carbon nanotube on said base by introducing the material gas containing the raw material for carbon installation in this reaction container in the condition have arranged the base which is the approach of growing up a carbon tube and formed a carbon nanotube growth initiation field beforehand on a front face on the base arranged in a reaction container in said reaction container, and generating the plasma by direct-current glow discharge in this reaction container.

[Claim 2] The manufacture approach of the carbon nanotube according to claim 1 which has arranged the anode plate which said base is the cathode for direct-current glow discharge, and counters this cathode in said reactor.

[Claim 3] The manufacture approach of carbon NANOBU according to claim 1 or 2 which the physical configuration or the chemical presentation was changed with other parts, and formed the carbon nanotube growth initiation field of said substrate.

[Claim 4] The manufacture approach of a carbon nanotube according to claim 1 to 3 that a carbon nanotube growth initiation field is an ultra-fine particle.

[Claim 5] The manufacture approach of a carbon nanotube according to claim 3 or 4 that a carbon nanotube growth initiation field contains one metal of Fe, Co, and nickel.
[Claim 6] The manufacture approach of a carbon nanotube according to claim 3 that a carbon nanotube growth initiation field consists of projection structure.
[Claim 7] The manufacture approach of a carbon nanotube according to claim 6 that said projection structure consists of needlelike structure.
[Claim 8] The manufacture approach of a carbon nanotube according to claim 1 to 7 that said material gas is the mixture containing the raw material and hydrogen for carbon installation.
[Claim 9] The manufacture approach of a carbon nanotube according to claim 1 to 7 that said material gas is the mixture containing the raw material and helium for carbon installation.
[Claim 10] The manufacture approach of the carbon nanotube according to claim 1 to 9 which is gas of the compound with which the raw material for said carbon installation consists of carbon and hydrogen.
[Claim 11] The manufacture approach of the carbon nanotube according to claim 1 to 10 which is the range whose pressure in said reaction container is 10-2-104 pascals.
[Claim 12] The manufacture approach of a carbon nanotube according to claim 1 to 11 that the direction of the electrical potential difference which carries out induction of said plasma is the growth direction of a carbon nanotube.
[Claim 13] The manufacture approach of a carbon nanotube according to claim 1 to 12 that the field strength of an average of the electrical potential difference which carries out induction of said plasma is 50 or more V/cm.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention is the range large as functional materials, such as an electron device and a micro device, a structural material, etc., and relates to the manufacture approach of an available carbon nanotube effectively especially as functional materials, such as probes, such as an electron emission ingredient and STM, a thin line for

micro machines, and a thin line for the quantum effectiveness components.
[0002]
[Description of the Prior Art] Although fibrous carbon is generally called the carbon fiber, as for the carbon fiber used as a structural material of a size with a diameter of several micrometers or more, many kinds of processes have been studied from the former. The process produced from the raw material of a PAN system or a pitch system occupies the current mainstream in it. The outlines of this process are non-deliquesce and the approach of fire-resistance-izing and carrying out high temperature processing at carbonization and 1500-3000 degrees C by 800-1400 degrees C about the raw material which carried out spinning from PAN fiber, the isotropic pitch, and the mesophase pitch. In this way, the obtained carbon fiber is excellent in mechanical properties, such as reinforcement and an elastic modulus, and since it is lightweight, it is used for sporting goods, a heat insulator, the structure material of aerospace relation or automobile relation, etc. also as a composite material.
[0003] The carbon nanotube discovered apart from this in recent years is the ingredient of the shape of a tube of a size with a diameter of 1 micrometer or less, and the field of a carbon hex-steel eye becomes parallel to the shaft of a tube, and it forms tubing. Furthermore, this tubing may become multiplex. It becomes metallic depending on how to roll a spiral, or becoming in semi-conductor is expected theoretically, and this carbon nanotube is expected as a future functional material.
[0004] It is as follows when the outline of the general manufacture approach of the textile materials of these carbon systems is summarized.
(1) Many kinds of things exist in a carbon fiber about a carbon fiber, and since it is known that the structure of the fiber compounded will change with a synthetic approach or its conditions a lot, the synthetic approach is chosen by the application etc. It is described by Michio Inagaki work "a new carbon ingredient" (technical ******) etc. for details.
[0005] Three kinds of main synthetic approaches are explained briefly below.
** A polyacrylonitrile is used for a PAN system carbon fiber raw material, and it is compounded through the three main processes, the spinning of a precursor, its non-deliquesce processing, and high temperature processing. In non-deliquesce processing and high temperature processing, cyclization, dehydrogenation by oxygen, and decarbonization-ized hydrogenation further accompanied by carbon hex-steel eye formation are performed. Moreover, by adding extension

actuation to a fiber in the middle of a process, a carbon hex-steel eye comes to arrange to the shaft orientations of a fiber, and it is known that a property will improve remarkably. In this way, there are general purpose (GeneralPurpose, GP) grade and a high intensity (High Tensile Strength, HT) type of the PAN system carbon fibers obtained.
** It is divided into the Lord of a mesophase system pitch based carbon fiber who indicates an anisotropy optically to be the isotropic pitch based carbon fiber built with an isotropic pitch to a pitch system carbon fiber pitch system carbon fiber by two kinds. The manufacture process is similar to the above-mentioned PAN system carbon fiber, and consists of carbonization by spinning, non-deliquesce processing, and high temperature processing.
[0006] Even if a mesophase system pitch based carbon fiber does not add extension actuation like [in the case of a PAN system carbon fiber], the good array of shaft orientations is acquired, and a radial (radial), random, coaxial-circles tubed (onion), etc. can also control the organization of a fiber cross section by viscosity of a pitch. A mesophase system pitch based carbon fiber is a rate (High Modulus, HM) type of high elasticity, and attracts attention as a future composite material. The isotropic pitch based carbon fiber belongs to GP grade, and is used for a heat insulator etc.
** a vapor growth system carbon fiber -- when one typical example is shown, it sends in in the electric furnace which made hydrogen carrier gas and held the benzene steam before and after 1050 degrees C, and there is a method of making it grow up on a substrate by making an iron particle into a catalyst. The growth process considers three kinds of the direction growth periods of a path which increase a size in nucleation, very thin growth of the shaft orientations of a fiber, and the direction of a path of a fiber. After the ultrafine particle of about 10nm iron is required for a catalyst and a fiber is obtained, Fe3C will exist at the tip of a fiber. It is thought that hydrogen gas also has reduction of iron and an operation of control of the pyrolysis of benzene.
[0007] The obtained fiber consists of the thick periphery section which arranges from a core almost in parallel with a hollow tube, a flat and thin mesh layer, and a shaft, and has an about 1nm mesh. An iron catalyst becomes a nucleus, the hollow tube which has a thin mesh layer by the flatness near a core is made, and the thick periphery section is considered to have been obtained by the pyrolysis of benzene. Such a tube is seen also when gaseous-phase pyrolysis of the carbon monoxide is carried out by making iron into a catalyst. G. G. Tibbetss is that the

same fiber is obtained even if it uses methane J. Crysi. Growth and 73 (1985) 431 It is explaining.
[0008] The seeding method which attaches the catalyst to the substrate in vapor growth (Seeding Catalyst Method) There is a fluid catalyst method (Floating Catalyst Method) make a catalyst float in a gaseous phase. By the fluid catalyst method, it is easy to become the configuration where the path of a fiber bent thinly. moreover, Ishioka ** -- **** of a fiber improves further that **** of a fiber improves by using the mixed gas of hydrogen and a 2 acid-number carbon carbon monoxide for carrier gas, and by using the mixture of a ferrocene and metal acetyl ASETETONEITO as a catalyst -- Carbon and 30 (1992) 859 And Carbon and 30 (1992) 865 It is setting and explaining.
[0009] When the fiber obtained by the seeding method adds heat treatment, a graphite-laminated structure progresses. That is, the network structure progresses near 2000 degree C, and the laminated structure of a mesh develops from near 2500 degree C. A graphite-laminated structure seldom progresses with the fiber created by the fluid catalyst method. If these fibers are heat-treated above 2800 degrees C, the polygonization from which a fiber outer wall becomes a polygon will occur.
[0010] If these processes are seen on the whole, fire-resistance-izing and non-deliquesce are required of a 150-400-degree C ambient atmosphere among air, and carbonization and graphitization need to be heat-treated of a PAN system and a pitch system also including vapor growth after that. That is, there are an ingredient of the carbonaceous carbonized by heat treatment near 1300 degree C and an ingredient of the graphite graphitized near 2800 degree C. A consistency increases with this heat-treatment and resistivity tends to decrease. By the ingredient, in general, a consistency, tensile strength, and a modulus of elasticity in tension increase in order of an isotropic pitch system, a PAN system, a mesophase pitch system, and a vapor growth system, and resistivity falls. In the isotropic carbon fiber, even if an average spacing performs elevated-temperature heat treatment by about 0.344nm, random layer structure remains. However, in a vapor growth system carbon fiber, if elevated-temperature heat treatment is performed above 2400 degrees C, an average spacing will be set to about 0.336nm, and an ideal laminated structure will be obtained. This can be evaluated also from measurement of a magnetic-reluctance value.
[0011] Although the path of the carbon fiber obtained by the process indicated above is several micrometers or more, when it compares in these, vapor growth can say that it is an ingredient near a carbon

nanotube that the laminating network structure parallel to a shaft is easy to be acquired.
(2) Although the common-name carbon nanotube and the call carbon fiber have distinguished the ingredient 1 micrometer or less with a diameter thinner than a carbon fiber about a carbon nanotube, there is no clear boundary. by this detail letter, it will have a configuration long and slender at a carbon fiber and a size with a diameter of 1 micrometer or less for the ingredient of a configuration long and slender at a size with a diameter of several micrometers or more, and the ingredient which the field of the hex-steel eye of carbon is parallel to the shaft orientations of fiber, and becomes tube-like will be called a carbon nanotube. However, also when amorphous carbon exists in the perimeter of a carbon nanotube, it includes in a carbon nanotube.
[0012] Two kinds are known by the current Lord at the process of a carbon nanotube. It is two kinds, a thermal decomposition method similar to the vapor growth of a carbon fiber, and an arc discharge method. The typical example of each approach is described briefly [below].
** The thermal decomposition method this gentleman method using a catalyst is almost the same as the vapor growth of a carbon fiber. C. E. SNYDER and others has indicated such a process to the international public presentation WO 89/07163. The material gas for carbon installation is introduced with hydrogen into a reaction container, and an ultra-fine particle is introduced into coincidence. As a raw material, the raw material which contains oxygen, such as unsaturated hydrocarbon, such as saturated hydrocarbon, such as methane, ethane, a propane, butane, a hexane, and a cyclohexane, ethylene, a propylene, benzene, and toluene, an acetone, a methanol, and a carbon monoxide, for example is used here. Moreover, as for the ratio of material gas and hydrogen, 1:20-20:1 are good, and the method of Fe independence or Fe, and the mixture of Mo, Cr, Ce, or Mn being recommended, and making it, as for a catalyst, adhere on a microparticulate (fumed) alumina is also advocated. In 550-850 degrees C, 200sccm extent has [the flow rate of gas] desirable material gas with which hydrogen contains 100sccm(s) and carbon per diameter of 1 inch, a reaction container introduces a particle, and a carbon tube grows in 30 minutes - about 1 hour.
[0013] In this way, the diameter of the configuration of the carbon tube obtained is about 3.5-75nm, and die length reaches by 5 to 1000 times the diameter. The network structure of carbon becomes parallel to the shaft of a tube, and there are few miscarriages of the pyrolysis carbon of a tube outside.
** An arc discharge method arc discharge method is first found out by

Iijima, and is indicated by Nature Vol.354 (1991) p.56-58 for details. An arc discharge method is a simple method of performing DC arc discharge using a carbon rod electrode in the ambient atmosphere of argon 100Torr. A carbon nanotube grows up to be a part of front face of a negative electrode with a 5-20nm carbon particle. This carbon tube is the layer structure with which the carbon mesh of the 2-50-fold shape of die length of about 1 micrometer and a tube lapped for the diameter of 4-30nm, and the network structure of that carbon is spirally formed in the shaft in parallel. Spiral pitches differ for every layer in every tube and a tube, and the distance between layers in the case of a multilayer tube is mostly in agreement with the distance between layers of 0.34nm and graphite. The tip of a tube is closed too in the network of carbon.

[0014] moreover, T.W.Ebbesen ** -- the conditions which generate a carbon nanotube in large quantities by the arc discharge method -- Nature Vol.358 (1992) -- it has indicated to p.220-222. The diameter of 9mm is used for cathode and a carbon rod with a diameter of 6mm is used for an anode plate, it installs so that it may detach 1mm and may counter in a chamber, and the arc discharge of about 18V and 100A is generated in the ambient atmosphere of about 500 helium Torr(s). If it is 500 or less Torrs, there will be few rates of a carbon nanotube and the whole amount of generation will decrease by at least 500 or more Torrs. The rate of the carbon nanotube in a product reaches to 75% in case of 500Torr(s) of optimum conditions. Even if it changed injection power or used the ambient atmosphere as the argon, the rate of collection of a carbon nanotube fell. Moreover, many nanotubes near the core of the generated carbon rod exist.

[0015] Since a multi-core tube and the tube of a monolayer are generally called a single tube for the thing of a multilayer tube for short here, an abbreviated name is used also in this specification.

[0016] When the above is summarized simply, as it is shown in drawing 1 , in a carbon fiber, it is parallel to a shaft, and parallel to a shaft at the core like [in the vapor phase cracking which has a configuration as shown in drawing 1 (a) from which the tube-like network structure has not developed, and used the catalyst] drawing 1 (b), and it is tube-like structure (it consists of carbon hex-steel eye structure.). the network structure -- un-illustrating -- the carbon of structure confused to the perimeter although it was -- many -- adhering -- **** -- an arc discharge method -- drawing 1 (c) -- like -- a core -- a shaft -- parallel -- and tube-like structure (it consists of carbon hex-steel eye structure.) The network structure is un-illustrating. It progresses and

there is also little coating weight of the carbon of the shape of amorphous [surrounding]. The sectional view in the case of the multi-core of this carbon nanotube is shown in drawing 1 d.

[0017]

[Problem(s) to be Solved by the Invention] By two kinds of both of the processes of the above-mentioned carbon nanotube, a size and the direction of the carbon nanotube obtained are random, and it is also mixing the carbon material of an impurity. The carbon nanotube obtained by this approach must be collected and refined after composition on the occasion of use, and it must form in a specific configuration according to the gestalt used further. When it is going to use as an electron source A. G. Rinzler and others is SCIENCE Vol. 269 (1995) p. 1550-1553. One of a carbon fiber is taken out as shown, and the electrical potential difference is drawing out the electron from the edge of the opposite side of the carbon nanotube which pastes up one of the two on an electrode, and exists in the core of a carbon fiber. moreover, Walt A. de Heer ** -- SCIENCE Vol. 270 (1995) -- p. 1179-1180 SCIENCEVol. 268 [and] (1995) -- as shown in p. 845-847, after refining the carbon nanotube produced by arc discharge, a tube is made to stand on a substrate using a ceramic filter, and the electron source is produced.

[0018] Although the direct carbon nanotube could be grown up on the base also with the thermal decomposition method using the catalyst of seeding, the direction of the carbon nanotube which needs to set up substrate temperature highly with about 800 degrees C, and grows cannot be controlled, either, but a size is also controlled, and amorphous-like carbon tended to grow up to be the peripheral wall of a ****** tube. Moreover, junction of a base and a carbon nanotube was also weak.

[0019] The high current was still more nearly required of arc discharge, and the temperature of the growth part of a carbon nanotube was very high, and it was impossible to have grown up a direct carbon nanotube on bases, such as a substrate of a quartz metallurgy group.

[0020] As mentioned above, it was very difficult to form a carbon nanotube in the direction considered as a request on the base which consists of the wide range quality of the material so that I might be understood, and growth at forming a carbon nanotube at intervals of a request further or low temperature was impossible. The purpose of this invention is to solve these troubles.

[0021] That is, the purpose of this invention is to offer the manufacture approach that a carbon nanotube may be comparatively grown up on a base at low temperature.

[0022] Other purposes of this invention are to offer the manufacture

approach that a carbon nanotube with a uniform property may be grown up on a base.
[0023] Other purposes of this invention are to offer the manufacture approach that the carbon nanotube with which directivity has been improved more on a base may be grown up.
[0024]
[Means for Solving the Problem] The above-mentioned technical problem is solvable with the following processes of this invention. That is, the manufacture approach of the carbon nanotube of this invention is in the condition which has arranged the base which formed the carbon nanotube growth initiation field in the front face beforehand in said reaction container, and is characterized by to form a carbon nanotube on said base by introducing the material gas containing the raw material for carbon installation in this reaction container, and generating the plasma by direct current glow discharge in this reaction container.
[0025] Although glow discharge is used for manufacture of a carbon nanotube in this invention, this glow discharge is clearly distinguished from arc discharge, and uses and explains drawing 2 about that difference below. Drawing 2 shows the current at the time of impressing the electrical potential difference of a direct current to inter-electrode [of positive/negative] in a suitable pressurized container, and the relation of an electrical potential difference. the field in [A] drawing -- a glow discharge field and high current side is called [B / a glow discharge field and] an abnormal-glow-discharge field to a low current side from a normal-glow-discharge field, a call, and it in the first half in an arc current field, and a call and the field for which the electrical potential difference in a glow discharge field hardly depends on a current still more finely. The part between a glow discharge field and an arc discharge field is called a transient. Glow discharge and arc discharge are described a little in more detail below.
** Glow discharge glow discharge is the discharge in which the discharge current was stabilized by the pressure in several 1000 pascals or less as for low voltage force several 10mA or less and low current. Such discharge is obtained with alternating voltage. In direct-current glow discharge, anode glow is in Aston dark space (it sees by helium with high excitation voltage, Ne, etc.), cathode glow, cathode dark space, negative glow, Faraday dark space and the positive column that occupies most, and the last from a cathode side. Most impressed electrical potential differences are concentrated near the cathode.
** In arc discharge arc discharge, an electrical potential difference decreases about to 1/10 compared with glow discharge, and a current is

large about 4-5 figures. Cathode was heated, so that it became white-hot, and since a thermoelectron is emitted so much from there, discharge sustaining voltage has fallen. It consists of an arc column of the cathode spot by the side of cathode, the anode spot of an anode plate edge, and the plasma state in the meantime in arc discharge.

[0026] The process in which a carbon nanotube is obtained in an arc discharge method is considered as follows. that is, carbon evaporates from the carbon electrode heated by arc discharge, and it ionizes in the plasma -- having -- the carbon ion C+ etc. -- it can draw near to cathode. In cathode, since it is an elevated temperature very much, it is in the situation that graphite-ization tends to take place. However, now, it is not clear why the configuration of a nanotube is easy to be acquired.

[0027] The former glow discharge method is used by the approach of this invention. It is almost impossible to use bases other than an electrode by the arc discharge method. With the approach of this invention, ion, such as carbon and a hydrocarbon, is built in the gas plasma, and a carbon nanotube is grown up by accelerating to cathode with an electrical potential difference, and supplying it by it.

[0028]

[Embodiment of the Invention] By the approach of this invention, what formed the carbon nanotube growth initiation field in the front face beforehand is first used as a base. What is necessary is to just be formed as this carbon nanotube growth initiation field as a part which can offer the part which is easy to make growth of a carbon nanotube start rather than other parts by changing a physical configuration and a chemical presentation with other parts, for example etc.

[0029] It can mention considering approaches, such as preparing the projection structure which enables concentration of an electrical potential difference as an approach of mentioning the approach of forming in a base the part of a presentation which may function, for example as a carbon nanotube growth initiation field as an approach of forming a carbon nanotube growth initiation field by change of chemical composition, and forming a carbon nanotube growth initiation field by change of a physical configuration, as a desirable thing. Thus, by preparing the carbon nanotube growth initiation field beforehand on the base, it becomes possible to control that the structure of the shape of amorphous carbon or graphite grows, and to promote growth of a carbon nanotube effectively.

[0030] As a carbon nanotube growth initiation field to which chemical composition was changed, what can form more effectively the part which

can be guided for growth initiation of a carbon nanotube can be used, for example, a metal or the semi-conductor of low resistance can be mentioned as a suitable thing. As these metals or a semi-conductor of low resistance, transition metals, such as Fe, Ti, V, Cr, Mn, Co, nickel, Cu, Nb, Mo, Pd, W, and Pt, a lanthanoids, SiC, etc. are mentioned. In these, alloys, such as Invar containing Fe, Co and nickel which are the metal catalyst which can promote the dehydrogenation of a hydrocarbon, or them, are more desirable.

[0031] The approach of, for example, making the ultrafine particle which consists of these ingredients fixing on a base as an approach of forming on a base the carbon nanotube growth initiation field which consists of these ingredients, the approach of forming in the front face of a base the part which consists of these ingredients, etc. can be mentioned.

[0032] As an approach of making it fix on a base as an ultrafine particle, the approach of spraying an ultrafine particle on a base front face can be used.

[0033] In addition, the ultrafine particle which consists of these ingredients can be obtained by the general approach called gas evaporation. That is, it is the approach of carrying out heating evaporation of the metal in inert gas, such as an about 104-pascal argon, using a crucible etc., and making it growing up to be an ultrafine particle in gas. It is also possible to also spray this generated. ultrafine particle on the base directly set to another chamber using differential pressure and for it to be possible, and to carry out distributed spreading on a base, once collecting ultrafine particles, or to spray. After forming a super-thin film for example, on a base besides such an approach, it is also possible by carrying out heating condensation to obtain an ultrafine particle.

[0034] By irradiating an electron ray on a base by SEM (Scanning Electron Microscope: scanning electron microscope) in which gas, such as some oil, exists as an approach furthermore controlled, it is possible to grow up a carbon ultrafine particle into the part. In this case, by changing gas into a raw material [**** / an organic metal etc.], it is also possible to grow up metals other than carbon.

[0035] In addition, there is the following general recognition about a "ultrafine particle." That is, a "particle", a call, and what is smaller than this are called a "ultrafine particle" for a small particle. It is performed widely that the number of atomic calls a "cluster" about hundreds of or less things still smaller than a "ultrafine particle." However, each boundary is not strict and it changes by paying attention to what kind of property it classifies. Moreover, a "particle" and a

"ultrafine particle" may be collectively called a "particle."
[0036] It is described as follows by "the experimental physics lecture 14 front face and the particle" (the volume on Koreo Kinoshita and KYORITSU SHUPPAN 1986 year 9 will publish for one day).
[0037] "When calling it a particle in this paper, the diameter carries out to from about 2-3 micrometers to about 10nm generally, and when calling it especially an ultrafine particle, particle size will mean from about 10nm to about 2-3nm. Since both are only collectively written to be particles, it is by no means strict, and they are most standards. In the case of dozens - about 100 numbers, the number of the atoms which constitute a particle calls it a cluster from two pieces. " (refer to the 22-26th 195-page line).
[0038] When added, the minimum of particle size was still smaller and that of the definition of the "ultrafine particle" in the Research Development Corporation of Japan" wood and ultrafine particle project" was as follows.
[0039] "In the "ultrafine particle project" (1981-1986) of a creation technology promotion system, it decided to call the thing of the range whose magnitude (path) of a particle is about 1-100nm a "ultrafine particle" (utlra fain particle). Then, one ultrafine particle is about 100-108. It will be called the aggregate of the atom like an individual. if it sees with an atomic scale, ultrafine particles will be size - a giant particle. what is still smaller than" (refer to two page 1 - 4th line volume [an ultrafine particle and "creation technology" wood Chikara, Ryoji Ueda, and on Tazaki ** , and the Mita publication / 1988 /) "ultrafine particle, i.e., an atom, -- some - one particle which consists of hundreds of pieces is usually called a cluster -- " (refer to this two-page writing of the 12-13th line) .
[0040] Although [in / based on the above general ways of calling / this specification / a "ultrafine particle"] the particle which has the particle size of the range of 1nm - several micrometers is pointed out, especially if the particle size of the ultrafine particle for the growth initiation fields of a carbon nanotube is extent which can enforce the approach of this invention, it will not be limited.
[0041] Furthermore, as an approach of not using an ultrafine particle, the approach of forming in a desired location the surface part which consists of the above-mentioned ingredient can be mentioned with the lithography technique by drawing of the light, ultraviolet rays, an X-ray, an electron ray, etc.
[0042] As an approach of producing the projection structure which can be used as a carbon nanotube growth initiation field to which the physical

configuration was changed on the other hand on a base front face, the process used by the electron source of FE (Field Emission: field emission) and the process used for production of the probe of STM (Scanning Tunneling Microscope: scanning tunneling microscope) are mentioned. The slanting vacuum evaporationo of the metal is carried out at this from on the hole of the resist which has an inverse tapered shape. Spindt who does lift off of the part of a hole -- law and the etching method which removes a mask after attaching the mask to the part which becomes a part for the point of a needle and performing side etching -- It is the imprint approach which attaches the mask to parts other than the part which becomes the hole of a substrate, performs anisotropic etching, makes a hole, considers as mold, forms a metal from on the, and removes a mold part.

[0043] The typical structure of the carbon nanotube growth initiation field obtained by the above approach is shown in drawing 3 . Drawing 3 (a) - (b) is what expressed the condition that the carbon nanotube growth initiation field 31 was formed on the base 32, as a typical sectional view. When drawing 3 (a) is formed using an ultrafine particle, drawing 3 (b) shows the case where drawing 3 (c) uses projection structure for the case where thin films, such as a metal which carried out pattern NINGU, are used for the shape of a predetermined dot using a lithography technique (when an acute angle [top-most vertices]), respectively.

[0044] As a base which can be used for the approach of this invention, various metal substrates, Si wafer, a quartz, glass, the ceramics, etc. are mentioned.

[0045] The base which formed the carbon nanotube growth initiation field as mentioned above is arranged in the predetermined location in the reaction container which can adjust internal pressure.

[0046] After exhausting the inside of a reaction container and making it about 10 - 6 pascals at reduced pressure in the place which arrangement of a base ended, the gas containing the raw material for carbon installation is continuously introduced in a reaction container. Although an introductory rate can be suitably chosen according to structure, a growth rate, etc. of a carbon nanotube which are considered as a request, it is desirable to adjust the introductory system of material gas and the exhaust air system of a reaction container, and to introduce material gas in a reaction container for example, so that the pressure in a reaction container may serve as range which is 10-2-104 pascals.

[0047] As a raw material for carbon installation introduced in a

reaction container, it is a compound containing carbon, and what can be introduced in the state of gas into a reaction container is available. For example, hydrocarbons, such as the methane which consists only of carbon and hydrogen, ethane, a propane, butane, a pentane, a hexane, ethylene, acetylene, benzene, toluene, and a cyclohexane, the benzonitrile containing other elements, an acetone, ethyl alcohol, methyl alcohol, a carbon monoxide, etc. are mentioned. Although a raw material desirable also in these changes a little with a presentation and growth temperature of the class of base, an ultrafine particle, etc., or pressures, an impurity does not enter [the direction of the raw material which consists of carbon and hydrogen] easily. Moreover, although at least these raw materials are [but] possible, it is more desirable to mix and use hydrogen, helium, etc.

[0048] In the place where the introductory condition into the reaction container of material gas is maintained, glow discharge is caused within a reaction container, the plasma is generated, and it is made to start from the carbon nanotube growth initiation field which prepared the carbon nanotube in the base front face beforehand.

[0049] In addition, base temperature can be chosen from the range of 400-900 degrees C, and optimum temperature is good to set up according to the presentation of a type of gas, gas pressure, and a growth initiation field etc.

[0050] It is possible to generate the glow discharge considered as a request as an electrode for this glow discharge generating, and it is [that there is especially no limit] available if growth of a carbon nanotube is not barred. Furthermore, it is desirable to choose and use the quality of the material and structure of a base so that the field of a base which has arranged the carbon nanotube growth initiation field at least may serve as the negative electrode in glow discharge. In this case, a positive electrode is installed in the location distant from the base front face a little. Although it depends for inter-electrode distance on the gas and the pressure to be used, it is several cm or less and considering as spacing which can discharge is desirable. Moreover, in order to arrange the growth direction of a carbon nanotube in the specific direction, as for the field strength of the average impressed to inter-electrode, it is effective that they are 50 or more V/cm. In addition, although the upper limit of this average field strength can be set up according to electrode structure, a type of gas, gas pressure, etc., it can be made into about 10 kV/cm extent, for example.

[0051] In addition, although the causal relation of the direction of

electric field and the growth direction of a carbon nanotube is not clear, complex causes, like that the conductivity of the shaft orientations of a carbon nanotube is large and it is [that ion such as C+, is concerned with growth or] easy to concentrate electric field at the tip of a tube can be considered.

[0052] According to the approach of this invention explained above, it has a diameter several nm - submicron, and the carbon nanotube of the die length of 10nm of long numbers - and 10 micrometers of numbers can be obtained. And since the one side [of a tube], i.e., base, side has already combined with the base, it is convenient for especially application that joins and uses only one side of nanotubes, such as probes, such as field electron emission and STM, and a trembler of a micro machine. It can apply, also when, joining both-sides junction and two or more electrodes, of course. Moreover, it is available also as reforming on front faces of a base, such as surface treatment, for example, surface inactivation processing, and high intensity-ized processing.

[0053]

[Example] An example is given to below and this invention is described in more detail.

The carbon nanotube was manufactured using the equipment shown roughly to example 1 drawing 4 .

[0054] In addition, the equipment shown in drawing 4 has the base electrode holder 44 (the heater (un-illustrating) is built in) for arranging the base 43 which serves both as the anode plate electrode 42 and cathode in the reaction container 41. Furthermore, the power source 45 for glow discharge generating can be connected now to the electrodes 42 and 43 in the reaction container 41, and the end connection with the material gas installation system 46 and the end connection with the exhaust air system 47 are prepared. In addition, although not illustrated, the temperature monitor of a base, the gas pressure measurement monitor, the pressure control valve, the gas flowmeter, etc. are installed. Moreover, it enables it to have adjusted inter-electrode distance to adjustable to 0.1-20mm with types of gas and a pressure.

[0055] Using the equipment shown in this drawing 4 , as it was the following, the carbon nanotube was manufactured.

[0056] First, the front face of Pd substrate as a base was made to distribute the ultrafine particle of a FeNi alloy (Fe0.5nickel0.5) with a diameter of about 20nm by heat-treatment so that it may be in the distributed condition of about ten - numbers on 1-micrometer square partly. In addition, this distributed condition can be attained also

with a vacuum evaporation process.
[0057] After installing this substrate on the base electrode holder 44, the reaction container 41 was exhausted to 10 - 6 pascals. Then, after heating a base electrode holder at 650 degrees C, the mixed gas of the ethylene, helium, and hydrogen which are material gas is introduced. The total pressure force after installation was made into 100 pascals, and the partial pressure of ethylene was made into 10 pascals. In this case, inter-electrode distance was set to 1cm. In this condition, 300V were impressed to the electrode, the plasma was generated, and it held for 30 minutes. And after ending electrical-potential-difference impression, intercepting a stop and gas supply for the plasma and making base temperature into the room temperature, it took out in atmospheric air. When the front face of taken-out Pd substrate was observed in FE-SEM (Field Emission-Scanning Electron Miciroscope: field emission scanning electron microscope), the carbon nanotube 51 of ten diameter as shown in drawing 5 (a) - 100nm of numbers was growing perpendicularly a little from the substrate 53, where one side of a tube is joined to a substrate 53. Moreover, it was few when it compared with growth of a carbon nanotube, although deposition of some amorphous carbon 52 was looked at by Pd of a substrate.
[0058] The Gabon nanotube was produced [example / secondary] with the equipment of the same drawing 4 as an example 1 using the ultrafine particle of various presentations.
[0059] What distributed partly the ultrafine particle which consists of any one sort in nickel, Fe, Co, Fe-nickel (Fe0.5nickel0.5), nickel-Co (nickel0.5Co0.5), and Au and Ag about ten - numbers on 1-micrometer square was prepared on the substrate front face of Pd like the example 1. Next, these substrates were used separately and the carbon nanotube by the equipment of drawing 4 was manufactured. That is, Pb substrate which gave the ultrafine particle beforehand was installed in base electrode-holder top 44 of the equipment shown in drawing 4 . And after exhausting a reaction container to 10 - 6 pascals, the base electrode holder was heated at 700 degrees C, and the mixed gas of the benzene, helium, and hydrogen which are material gas was introduced. The total pressure force after installation made the partial pressure of benzene 10 pascals as 100 pascals. In addition, inter-electrode distance was set to 1cm. And 300V were impressed to the electrode, the plasma was generated, and it held for 30 minutes. And when it took out in atmospheric air and the front face of taken-out Pd substrate was observed in FE-SEM after ending electrical-potential-difference impression, intercepting a stop and gas supply for the plasma, and making temperature of a substrate into the

room temperature, on nickel, Fe, Co, Fe-nickel, and Pd substrate that distributed the ultrafine particle of nickel-Co, the carbon nanotube of ten diameter as shown in drawing 5 (a) - 100nm of numbers was growing perpendicularly a little from the substrate. It was few when it compared with growth of a carbon nanotube, although deposition of some amorphous carbon was looked at by Pd of a substrate at this time.

[0060] However, on Pd substrate which distributed the ultrafine particle of Au and Ag, although deposition of some amorphous carbon was seen, most growth of a carbon nanotube was not accepted.

[0061] The example which produced the growth part of a carbon nanotube using the example 3, next the lithography technique, etc. is explained.

[0062] First, Ti was thinly formed upwards on the quartz substrate (20nm of thickness), and Pt was formed by the spatter (40nm of thickness). Furthermore, nickel of 10nm thickness was formed on it, and this nickel thin film layer was processed by the electron-beam lithography method and the general exposing method in the shape of [of about 50nm - 10 micrometer angle] a dot (spacing of each dot: about 10 times of the diameter of a dot).

[0063] Moreover, apart from this, the dot (spacing of each dot: about 10 times of the diameter of a dot) of the carbon of 10nm angle of numbers was formed in the front face of the quartz substrate in which Pt thin film (40nm of thickness) was formed, by applying an electron ray to some substrates in SEM of an ambient atmosphere with some carbon source (CH4 or oil).

[0064] In this way, two sorts of obtained substrates were used separately, respectively, and the carbon nanotube by the equipment of drawing 4 was manufactured. That is, the substrate which prepared the thin film of the shape of a metaled dot beforehand was used as the base, and it installed on the base electrode holder 44 of the equipment of drawing 4 , after exhausting a reaction container to 10 - 6 pascals, the base electrode holder was heated at 300 degrees C, and the acetylene, helium, and hydrogen which are material gas were introduced. The total pressure force after installation made the partial pressure of acetylene 5 pascals as 500 pascals. In addition, inter-electrode distance was set to 1cm. And 200V were impressed to the electrode, the plasma was generated, and it held for 30 minutes. And after ending electrical-potential-difference impression, intercepting a stop and gas supply for the plasma, and making substrate temperature into the room temperature, it took out in atmospheric air. When Pt thin film front face was observed in FE-SEM on the front face of the taken-out quartz substrate, on the substrate into which a substrate [in which the carbon dot was

formed] top, and nickel were processed in the shape of [below 1 micrometer angle] a dot, the carbon nanotube of ten diameter as shown in drawing 5 (a) - 100nm of numbers was growing perpendicularly a little from the substrate. It was few when it compared with growth of a carbon nanotube, although deposition of some amorphous carbon was looked at by Pt of a substrate at this time.

[0065] The example which produced the needlelike growth part using the example 4, next the lithography technique, etc. is explained.

[0066] First, Ti was thinly formed upwards on the quartz substrate (20nm of thickness), and Pt was formed by the spatter (40nm of thickness). The resist (trade name: RD2000; Hitachi Chemical Co., Ltd.) was applied on it, and the hole which has an inverse tapered shape with a diameter of several micrometers by the usual lithography method for patterning of a metal thin film was made. Co was formed by the oblique incidence method from besides, and conic Co projection structure as shown in drawing 3 (c) was produced on the substrate front face by removing a resist after that.

[0067] In this way, the obtained substrate was used as the base and it installed on the base electrode holder 44 of the equipment shown in drawing 4 , after exhausting a reaction container to 10 - 6 pascals, the base electrode holder was heated at 600 degrees C, and the benzene and hydrogen which are material gas were introduced. The total pressure force after installation was made into 500 pascals, and the partial pressure of benzene was made into 50 pascals. In addition, inter-electrode distance was set to 1cm. And 200V were impressed to the electrode, the plasma was generated, and it held for 30 minutes. And after ending electrical-potential-difference impression, intercepting a stop and gas supply for the plasma, and making substrate temperature into the room temperature, it took out in atmospheric air. When Pt thin film front face of the taken-out quartz substrate was observed in FE-SEM, several 100nm carbon nanotube as shown in drawing 5 (b) was growing almost perpendicularly from the substrate. It was few when it compared with growth of a carbon nanotube, although deposition of some amorphous carbon was looked at by Pt of a substrate at this time.

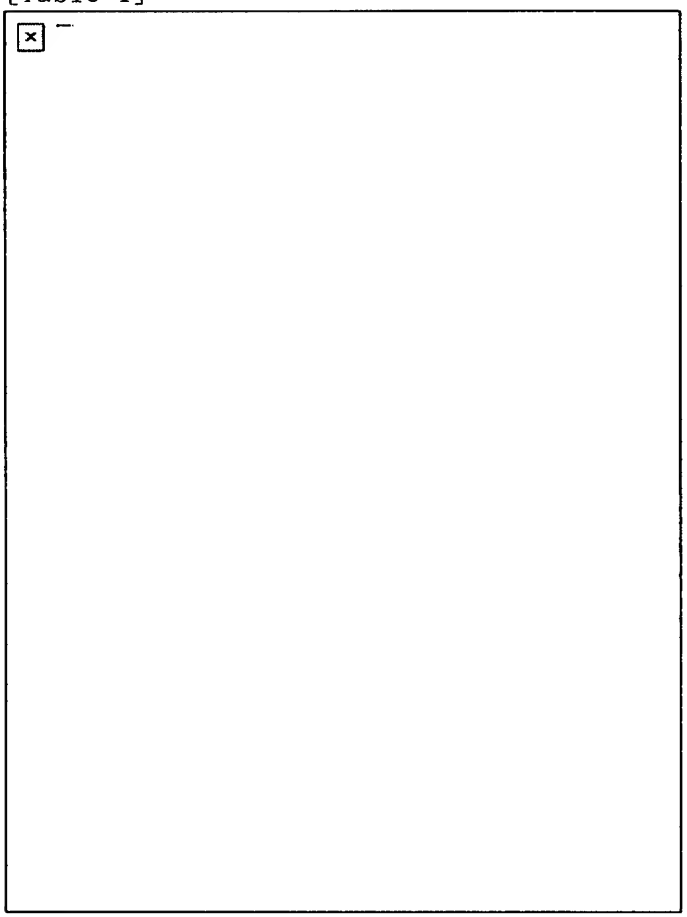
[0068] The carbon nanotube was produced using various gas with the equipment of the same drawing 4 as an example 5, next an example 1.

[0069] The ultrafine particle of Fe-nickel was partly distributed about ten - numbers on 1-micrometer square on the substrate of Pd like the example 1, and it installed on the base electrode holder 44 of the equipment shown in drawing 4 . And after exhausting a reaction container to 10 - 6 pascals, the base electrode holder was heated at 750 degrees C,

and A which is material gas, and the other gas B were introduced. The class and combination of Gas A and Gas B are as being shown in the following table 1. In addition, inter-electrode distance was set to 1cm.

[0070]

[Table 1]



And the total pressure force after installation was made into 100 pascals, and the partial pressure of Gas A was made into 10 pascals. After reaching the pressure of a setup, 300V were impressed to the electrode, the plasma was generated, and it held for 30 minutes. And after ending electrical-potential-difference impression, intercepting a stop and gas supply for the plasma, and making substrate temperature into the room temperature, it took out in atmospheric air. The front face of taken-out Pd substrate was observed in FE-SEM. Consequently, although the carbon nanotube of ten diameter as shown in drawing 5 (a) also in the combination of which above-mentioned gas - 100nm of numbers had grown to be a substrate When it was material gas No. 5-10 (material gas consists of hydrogen and carbon and helium and hydrogen are

introduced in addition to it), the carbon nanotube was especially thin, network structure parallel to a shaft was acquired finely, and there was also little deposition of the amorphous carbon to Pd top of a substrate.
[0071] The glow discharge electrical potential difference was changed with the equipment of the same drawing 4 as an example 6, next an example 1, and the carbon nanotube was produced.
[0072] Like the example 1, the ultrafine particle of Fe-nickel was partly distributed about ten - numbers on 1-micrometer square on the substrate of Pd, and it installed in the base electrode holder 44 of drawing 4 by making this into a base. And after even 10 - 6 pascals even of reaction containers exhausted, the base electrode holder was heated at 600 degrees C, and the acetylene, helium, and hydrogen which are material gas were introduced. The total pressure force after installation was made into 10-2-104 pascals, and the partial pressure of acetylene was set to 1/10 of the total pressure force. And according to the total pressure force, 100-1000V, and inter-electrode distance were adjusted for the electrical potential difference to 0.1-20mm, the plasma was generated, and it held for 10 - 100 minutes. And after ending electrical-potential-difference impression, intercepting a stop and gas supply for the plasma, and making substrate temperature into the room temperature, it took out in atmospheric air. When the front face of taken-out Pd substrate was observed in FE-SEM, the direction of conditions 50v [/mm] or more was in the inclination for the carbon nanotube of the diameter 10 as the field strength of an inter-electrode average shows to drawing 5 (b) - 100nm of numbers to grow perpendicularly mostly from a substrate, and on conditions 50v [/mm] or less, average field strength came to show drawing 5 (a), and, as for the inclination to grow up to be the substrate of a carbon nanotube perpendicularly, became weaker.
[0073]
[Effect of the Invention] According to this invention, at comparatively low base temperature, a direct carbon nanotube can be formed in a base and it becomes possible to expand the width of face of selection of the quality of the material of a base. Furthermore, according to this invention, by choosing manufacture conditions, a property is uniform and it becomes possible to manufacture the carbon nanotube with which the directivity of growth has been improved more. Moreover, according to this invention, the unnecessary carbon nanotube of purification processing can be offered. Furthermore, since the carbon nanotube obtained by this invention is offered after the end has combined with the base, and it can moreover be formed by using a base as an electrode

with the quality of the material in which a function is possible, it is available as an electronic functional material as it is in this.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing the structure of a carbon fiber and a carbon nanotube typically, and the sectional view in the fiber shaft orientations of a carbon nanotube and (d of the sectional view in the fiber shaft orientations of the pyrolysis for which (a) used the sectional view in the isotropic fiber shaft orientations of a carbon fiber for, and (b) used the catalyst, and the carbon fiber obtained by vapor growth, and (c)) are the sectional views in a direction perpendicular to the fiber axis of a multi-core carbon nanotube.
[Drawing 2] It is the correlation diagram of the current in glow discharge and arc discharge, and an electrical potential difference.
[Drawing 3] It is drawing showing the structure of the growth initiation field of the carbon nanotube formed in the base front face, and drawing showing the growth initiation field formed in the metaled minute field, and (c) are [(a)] drawing the growth initiation field which consists of a needlelike projection is shown in drawing showing the growth initiation field which was made to carry out surface distribution and obtained the ultrafine particle, and (b).
[Drawing 4] It is the schematic diagram of the manufacturing installation of a carbon nanotube.
[Drawing 5] It is the schematic diagram of the carbon nanotube which grew on the base, and drawing in which (a) shows the growth condition of a carbon nanotube with comparatively little directivity, and (b) are drawings showing the growth condition of a carbon nanotube that the direction gathered comparatively.
[Description of Notations]
31 Carbon Nanotube Growth Part
32 Base
41 Reaction Container
42 Anode Plate Electrode
43 Base and Cathode Electrode
44 Base Electrode Holder and Heater
45 Power Source

46 Gas Feed System
47 Exhaust Air System
51 Carbon Nanotube
52 Base Front Face
53 Base